

Claims

- 5           1.     A chromium(VI)-free, chromium(III)-containing and  
              substantially coherent conversion layer on zinc or zinc alloys,  
  
              **characterised in that**  
  
10           even in the absence of further components such as silicate,  
              cerium, aluminum and borate it presents a corrosion  
              protection of approx. 100 to 1000 h in the salt spray test  
              according to DIN 50021 SS or ASTM B 117-73 until first  
              attack according to DIN 50961 Chapter 10;  
  
15           it is clear, transparent and essentially colorless and presents  
              multi-colored iridescence;  
  
              it has a layer thickness of approx. 100 nm to 1000 nm; and  
  
20           it is hard, adheres well and is resistant to wiping.
2.     A conversion layer according to claim 1, characterised in that  
              it has across the conversion layer thickness a chromium  
25           content of up to approx. 1%, in relation to zinc and chromium  
              in the conversion layer an average chromium content of more  
              than approx. 5%;  
  
              it has a chromium-rich zone > approx. 20% chromium, in  
30           relation to zinc and chromium in the conversion layer, of more  
              than approx. 15 nm; and  
  
              it has a chromium index > approx. 10.
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              that it may contain, for further enhanced corrosion protection,

additional components selected from the group consisting of:  
silicate, cerium, aluminum and borate;

5 additional metal compounds, in particular 1- to 6-valent metal  
compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe,  
Ga, In, lanthanides, Zr, Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo,  
Hf, Ta, W; and

10 anions, in particular halide ions, in particular chloride ions;  
sulfurous ions, in particular sulfate ions, nitrate ions;  
phosphoric ions, in particular phosphate ions, diphosphate  
ions, linear and/or cyclic oligophosphate ions, linear and/or  
cyclic polyphosphate ions, hydrogen phosphate ions;  
15 carboxylic acid anions; and silicon-containing anions, in  
particular silicate anions; and

20 polymers, in particular organic polymers, corrosion inhibitors;  
silicic acids, in particular colloidal or disperse silicic acids;  
surfactants; diols, triols, polyols; organic acids, in particular  
monocarboxylic acids; amines; plastics dispersions; dyes,  
pigments, in particular carbon black, chromogenic agents, in  
particular metallic chromogenic agents; amino acids, in  
particular glycine; siccatives, in particular cobalt siccatives;  
dispersing agents; and

25 mixtures thereof.

30 4. A conversion layer according to any one of claims 1 to 3,  
characterised in that it is a basis for further inorganic and/or  
organic layers.

5. A conversion layer according to any one of claims 1 to 4,  
characterised in that it contains dyes or color pigments for  
modification of the inherent color thereof.

35 6. A conversion layer according to any one of claims 1 to 5,  
characterised in that its layer thickness is approx. 100 nm.

7. A method for producing chromium(VI)-free conversion layers affording at least the corrosion protection of conventional chromium(VI)-containing yellow chromations, wherein

a metallic surface, in particular one of zinc or zinc alloys, in particular with iron, is treated with a solution of at least one chromium(III) complex and at least one salt;

**characterised in that**

the concentration of the chromium(III) complex is increased in comparison with a conventional trivalent blue chromation; and/or

a chromium(III) complex is used having ligand replacement kinetics more rapid than the fluoride replacement kinetics in chromium(III)-fluorocomplexes.

8. A method according to claim 7, characterised in that treatment is carried out at an elevated temperature, in particular 20 to 100°C, preferably 20 to 80°C, in a preferred manner 30 to 60°C, in a particularly preferred manner 40 to 60°C.

9. A method according to any one of claims 7 or 8, characterised in that the ligands of the chromium(III) complex are selected from the group consisting of:

chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and

furthermore, maleic acid, phthalic acid, terephthalic acid, tartaric acid, citric acid, malic acid, ascorbic acid; and

further chelate ligands such as acetylacetone, urea, urea derivatives, and

further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur ( $-NR_2$ ,  $-PR_2$ , wherein R independently is an organic, in particular aliphatic radical and/or H, and/or  $-SR$ , wherein R is an organic, in particular aliphatic radical or H); phosphinates and phosphinate derivatives; as well as

suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and  $H_2O$  and/or

the method is performed repeatedly on the surface to be passivated.

10. A concentrate for producing a passivation solution for surfaces of zinc or zinc alloys, in particular ones with iron, wherein it substantially contains chromium(III) for a passivating component,

**characterised in that**

the chromium(III) is present in the form of at least one complex having ligand replacement kinetics more rapid than the fluoride replacement kinetics in chromium(III)-fluorocomplexes.

11. A concentrate according to claim 10, characterised in that the chromium(III) complex is selected from complexes with chromium(III) and at least one ligand from the group consisting of:

chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and

furthermore, maleic acid, phthalic acid, terephthalic acid, tartaric acid, citric acid, malic acid, ascorbic acid; and

5 further chelate ligands such as acetylacetone, urea, urea derivatives, and

10 further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur ( $-NR_2$ ,  $-PR_2$ , wherein R independently is an organic, in particular aliphatic radical and/or H, and/or  $-SR$ , wherein R is an organic, in particular aliphatic radical or H,); phosphinates and phosphinate derivatives; as well as

15 suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and  $H_2O$ .

12. A concentrate according to any one of claims 10 or 11, characterised in that the concentrate is present in solid or  
20 liquid form.

13. A concentrate according to any one of claims 10 to 12, characterised in that it contains further additives selected from the group consisting of: sealers, dewatering fluids; and

25 additional metal compounds, in particular 1- to 6-valent metal compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe, Ga, In, lanthanides, Zr, Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo, Hf, Ta, W; and

30 anions, in particular halide ions, in particular chloride ions; sulfurous ions, in particular sulfate ions, nitrate ions; phosphoric ions, in particular phosphate ions, diphosphate ions, linear and/or cyclic oligophosphate ions, linear and/or  
35 cyclic polyphosphate ions, hydrogen phosphate ions; carboxylic acid anions; and silicon-containing anions, in particular silicate anions; and

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polymers, in particular organic polymers, corrosion inhibitors;  
silicic acids, in particular colloidal or disperse silicic acids;  
surfactants; diols, triols, polyols; organic acids, in particular  
monocarboxylic acids; amines; plastics dispersions; dyes,  
pigments, in particular carbon black, chromogenic agents, in  
particular metallic chromogenic agents; amino acids, in  
particular glycin; siccatives, in particular cobalt siccatives;  
dispersing agents; as well as

mixtures thereof.

14. A passivation bath for passivating metal surfaces, in particular  
ones of zinc, cadmium or aluminum, or alloys of these metals  
among each other and/or with other metals, in particular with  
iron,

**characterised in that**

it substantially contains chromium(III) as a passivating  
component, wherein chromium(III) is present in a  
concentration of approx. 5 to 100 g/l.

15. A passivation bath according to claim 14, characterised in that  
chromium(III) is present in a concentration of approx. 5 g/l to  
80 g/l, in particular of approx. 5 g/l to 60 g/l, in a particularly  
preferred manner of approx. 10 g/l to 30 g/l, preferably  
approx. 20 g/l.

16. A passivation bath according to claim 14 or 15, characterised  
in that it has a pH between approx. 1.5 and 3.

17. A passivation bath according to any one of claims 14 to 16,  
characterised in that it contains approx. 20 g/l chromium(III)  
and has a pH of approx. 2 to 2.5.

18. A passivation bath according to any one of claims 14 to 17, characterised in that it contains further additives in particular selected from the group consisting of sealers, dewatering fluids: and

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additional metal compounds, in particular 1- to 6-valent metal compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe, Ga, In, lanthanides, Zr, Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo, Hf, Ta, W; and

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anions, in particular halide ions, in particular chloride ions; sulfurous ions, in particular sulfate ions, nitrate ions; phosphoric ions, in particular phosphate ions, diphosphate ions, linear and/or cyclic oligophosphate ions, linear and/or cyclic polyphosphate ions, hydrogen phosphate ions; carboxylic acid anions; and silicon-containing anions, in particular silicate anions; and

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polymers, corrosion inhibitors; silicic acids, in particular colloidal or disperse silicic acids; surfactants; diols, triols, polyols; organic acids, in particular monocarboxylic acids; amines; plastics dispersions; dyes, pigments, in particular carbon black, chromogenic agents, in particular metallic chromogenic agents; amino acids, in particular glycine; siccatives, in particular cobalt siccatives; dispersing agents; as well as

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mixtures thereof.

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19. A passivation bath according to any one of claims 14 to 18, characterised in that it has a bath temperature of approx. 20 to 100°C, preferably 20 to 80°C, in a preferred manner 30 to 60°C, in a particularly preferred manner 40 to 60°C.

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20. A method for passivating surfaces of zinc or zinc alloys, in particular ones with iron,

**characterised in that**

the objects to be treated are immersed in a passivation bath according to any one of claims 14 to 19.

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21. A method according to claim 20, characterised in that the immersion period is between approx. 15 and 200 seconds, in particular between approx. 15 and 100 seconds, preferably approx. 30 seconds.

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22. A method according to any one of claims 20 or 21, characterised in that it is an elevated-temperature chromate coating method with rinsing water recycling over at least 2 cascaded rinsing stages.

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23. A method according to claim 22, characterised in that a blue chromation is performed in one of the rinsing steps.

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24. A passive layer obtainable by a method according to at least one of claims 20 to 23.

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25. A passive layer according to claim 24, characterised in that it imparts a corrosion protection to an object such as to present a corrosion protection of at least 100 hours in the salt spray test according to DIN 50021 SS until first attack according to DIN 50961 Chapter 10.

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26. A passive layer according to claim 24 or 25, characterised in that it presents a greenish, red-green iridescent color for zinc.

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27. A passive layer according to any one of claims 24 to 26, characterised in that its layer thickness is approx. 100 nm.
28. A conversion layer obtainable by a method according to at least one of claims 7 to 9.